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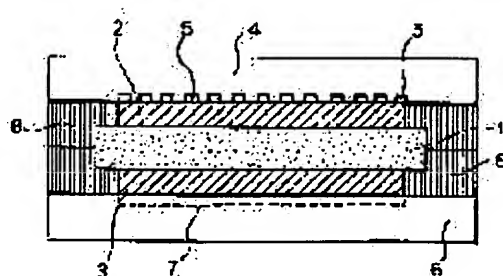
(54) POLYMER SOLID ELECTROLYTE FUEL CELL

(57)Abstract:

PURPOSE: To provide a polymer solid electrolyte fuel cell of which ion conductivity is improved by lowering the specific resistance of an ion exchange membrane and in which water control can be carried out so as to allow of no- humidification operation.

CONSTITUTION: In a solid electrolyte fuel cell comprising a collector 1 for a cathode, a catalytic layer 2 for the cathode, an ion exchange membrane 3, a catalytic layer 4 for an anode, and a collector 5 for the anode which are united, finely granulated silica and/or fibrous silica fiber is added to the catalytic layer 1 for the cathode and the catalytic layer 4 for the anode.

Consequently, the specific resistance of the fuel cell is lowered and the ion conductivity is improved and at the same time no-humidification operation can be carried out.



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CLAIMS

[Claim(s)]

[Claim 1] The solid polymer electrolyte mold fuel cell which the laminating of the charge collector for cathodes, the catalyst bed for cathodes, ion exchange membrane, the catalyst bed for anodes, and the charge collector for anodes is carried out, and is characterized by the silica and/or the fibrous silica fiber of a very fine particle containing in one of them at least among said ion exchange membrane, the catalyst bed for cathodes, and the catalyst bed for anodes in the solid electrolyte fuel cell with which a oxidizing gas is supplied to said catalyst bed for cathodes, and fuel gas is supplied to said catalyst bed for anodes.

[Claim 2] Said silica fiber is the solid polymer electrolyte mold fuel cell of claim 1 characterized by a size being 6 micrometers or less while the first [an average of] grain size of said silica is 0.1 micrometers or less.

[Claim 3] The silica in said ion exchange membrane and/or the content of a silica fiber are the solid polymer electrolyte mold fuel cell of claim 1 characterized by being 0.01 - 50 % of the weight to the weight of an ion exchange membrane.

[Claim 4] The silica of said catalyst bed for cathodes and the catalyst bed for anodes and/or the content of a silica fiber are the solid polymer electrolyte mold fuel cell of claim 1 characterized by being 0.0006 - 31 % of the weight to the weight of a catalyst tub.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to amelioration of the cell engine performance of a solid polymer electrolyte mold fuel cell of having ion exchange membrane.

[0002]

[Description of the Prior Art] A fuel cell transforms chemical energy, such as natural gas, into electrical energy directly by the chemical reaction, and has the big description that generating efficiency is cleanly high compared with other generators (a gas engine, a gas turbine, diesel power plant, etc.).

[0003] Although there are a phosphoric-acid mold, an alkali water-solution mold, a melting carbonate mold, a solid oxide type, a solid polymer electrolyte mold, etc. in the class of fuel cell, since the solid polymer electrolyte mold fuel cell about this invention can take out compact and high current density compared with other fuel cells, it attracts attention as a power source for an electric vehicle and spacecrafts. And the cell engine performance of this solid polymer electrolyte mold fuel cell is greatly governed by the factor shown below.

(1) Ion exchange membrane is that ion conductivity is good. That is, ion conductivity becomes good and can obtain high current density, so that the specific resistance of the ion exchange membrane itself is small. Increasing from this the concentration of the ion exchange group in solid polymer electrolytes, such as fluorination resin, such as hydrocarbon system ion-exchange resin which is the film material of ion exchange membrane, or Nafion (trade name -- perfluorocarbon sulfonic acid which U.S. Du Pont developed), as the ion conductivity amelioration approach of ion exchange membrane is proposed. Or the attempt which improves the ion conductivity of ion exchange membrane is also made by machining the film.

(2) Moisture management of ion exchange membrane, an anode, and a cathode be proper. That is, if ion exchange membrane dries, the ion conductivity falls remarkably, the internal resistance of a cell will increase and the cell engine performance will fall. Moreover, when it sees about the moisture condition of an anode and a cathode, the inside of ion exchange membrane is faced to a cathode from an anode, and it is H^+ . It is H^+ that the moisture by the side of an anode runs short, and it is easy to dry in order that ion may accompany a water molecule. Migration of ion is reduced. On the other hand, in a cathode side, if the water generated by electrode reaction becomes superfluous, the inflow of reactant gas will be barred and smooth electrode reaction will be checked. For this reason, in an anode side, it is required to humidify, to dehumidify in a cathode side and to maintain moisture proper. That is, the cell engine performance can be raised from performing moisture management of ion exchange membrane, an anode, and a cathode proper. The approach of humidifying an ion exchange membrane through fiber is proposed by making it an ion exchange membrane on both sides of ****-like fiber as one of the cures against moisture management at sandwich structure from this. Moreover, the approach of humidifying ion exchange membrane indirectly as another cure by humidifying the reactant gas by the side of an anode with a steam is proposed.

[0004]

[Problem(s) to be Solved by the Invention] However, when the concentration of the ion exchange group of a solid polymer electrolyte is increased, hydrocarbon system ion exchange resin has the problem that the softness which is the description of a macromolecule is lost, junction of ion exchange membrane, an anode or ion exchange membrane, and a cathode becomes difficult, and manufacture of a fuel cell becomes difficult. Moreover, in the case of fluorination resin, such as Nafion, in order that the film may fluidize, there is a problem [installation / of many ion exchange groups] of being difficult, technically. [0005] Moreover, if thickness of ion exchange membrane is made thin, the mechanical strength of the film itself will become small, and there is a problem of being easy to damage ion exchange membrane. Therefore, current and the ion conductivity of the ion exchange membrane which can be used should not be satisfied, and ion conductivity good ion exchange membrane is demanded. Since thickness becomes thick and only the part which makes it sandwiches on both sides of fiber although the approach of on the other hand making it into the structure which sandwiched ****-like fiber in the cure against moisture management can perform humidification to an ion exchange membrane causes an ion conductivity fall, it cannot become fundamental solution easily. Moreover, since diffusion of the reactant gas in an electrode catalyst bed is also checked while causing the partial pressure fall of reactant gas, since reactant gas is diluted by the steam, the approach of humidifying reactant gas with a steam becomes the factor to which the cell engine performance falls. Furthermore, since it is difficult to fluctuate the amount of the steam followed and humidified for the load to change, the film dries, without the ability supplying moisture enough, or a catalyst bed is wet too much conversely, and there is a problem of reducing the cell engine performance.

[0006] While this invention was made in view of such a situation, can make specific resistance of ion exchange membrane small and being able to improve ion conductivity, it aims at offering the solid polymer electrolyte mold fuel cell which can perform moisture management in which non-humidified operation is possible.

[0007]

[Means for Solving the Problem] If this invention is outlined, this invention will be invention which improves the cell engine performance of a solid polymer electrolyte mold fuel cell, and it will be characterized by the silica and/or the fibrous silica fiber of a very fine particle containing in one of them at least among said ion exchange membrane, the catalyst bed for cathodes, and the catalyst bed for anodes in the solid polymer electrolyte mold fuel cell with which the laminating of the charge collector for cathodes, the catalyst bed for cathodes, ion exchange membrane, the catalyst bed for anodes, and the charge collector for anodes was carried out.

[0008] As this invention persons were shown in Table 1, while, as for the solid polymer electrolyte (Nafion is used) which the silica and/or the silica fiber contained, ion conductivity was improved by specific resistance becoming small, it found out raising water content. And when the silica and/or the fibrous silica fiber of a very fine particle contain in one of them at least based on this among ion exchange membrane, the cathode catalyst bed, and the anode catalyst bed, the cell engine performance of a solid polymer electrolyte mold fuel cell is raised.

table 1 Water content and specific resistance of a solid polymer electrolyte 80 degrees (omegacm) of silica content (%) water content (%) specific resistance C 0.00 2.5 10.5 0.01 20.0 10.0 0.10 28.0 7.4 1.00 31.0 5.5 3.00 - 5.4 10.00 34.0 6.020.00 - 6.8 30.00 - 7.5 50.00 - In 9.8 (note) table 1, although the silica of a very fine particle was used, the result with the same said of a fibrous silica fiber was obtained.

[0009] That is, according to the solid polymer electrolyte mold fuel cell of this invention, in the ion exchange membrane, the silica and/or the fibrous silica fiber of a very fine particle contain. Thereby, since specific resistance of the ion exchange membrane itself can be made small, the ion conductivity of ion exchange membrane is improved and the cell engine performance can be raised. And the cluster structure model of the giant-molecule solid electrolyte which constitutes the film can explain why the ion conductivity of the ion exchange membrane itself is improved by content of said silica and/or a silica fiber. That is, ion exchange group comrades gather, and the ionic conduction device of a solid polymer electrolyte forms about 4nm space, and is connected with the communicating tube this space comrade of whose is about 1nm. And when water exists in said space, it is supposed that migration of ion will take.

place. On the other hand, a particle, i.e., the silica of high specific surface area, shows high hygroscopicity. From this, when a silica and/or a silica fiber contain in an ion exchange membrane, the abundance of the water in said space increases and it is thought that the ion conductivity of an ion exchange membrane is improved.

[0010] Moreover, since water capacity which can hold the whole ion exchange membrane when a silica and/or a silica fiber contain can be enlarged, desiccation of ion exchange membrane can be prevented. Furthermore, when a silica fiber contains, the mechanical strength of ion exchange membrane can be enlarged. Since damage on membranous cannot break out easily by this even if it makes thickness of ion exchange membrane thin, ion conductivity is improvable by making thickness thin.

[0011] In this invention, the silica of the very fine particle to contain has the crystal structure of amorphism, and its 0.01 micrometers or less are [the first / an average of / grain size] preferably desirable 0.1 micrometers or less. Moreover, as for a silica fiber, it is desirable for a size to be 5 micrometers or less. Because, when a silica and a size 0.1 micrometers or more are a silica fiber 5 micrometers or more, the effectiveness of reducing the specific resistance of ion exchange membrane does not have the first [an average of] small practical grain size. Moreover, as a content, it is 0.01 - 50 % of the weight to the weight of a solid polymer electrolyte, and it is desirable that it is 0.1 - 20 % of the weight preferably. Because, as shown in said table 1, the content of the silica contained in a solid polymer electrolyte is no longer accepted for the amelioration effectiveness of specific resistance at 0.01 or less % of the weight or 50 % of the weight or more. Moreover, if a silica and/or a silica fiber, and ion-exchange resin are mixed in the condition of having made it suspending and dissolving in the solvent of hydrophilic properties, such as a methanol, ethanol, isopropanol, and a butanol, respectively when making an ion exchange membrane contain a silica and/or a silica fiber, since the specific resistance of an ion exchange membrane will become small, it is desirable. As this reason, it is presumed by using the solvent of a hydrophilic property that the silica to contain becomes that it is easy to contain where said cluster structure formed by the ion exchange group (hydrophilic property) of a solid polymer electrolyte is approached.

[0012] Moreover, as a solid polymer electrolyte which is the film material of ion exchange membrane, the cation exchange resin of the perfluorocarbon sulfonic acid used for various electrochemistry equipments as ion exchange membrane, Pori Sall John, a perfluoro carboxylic acid, and styrene - vinylbenzene sulfonic acid, a styrene-butadiene system anion exchange resin, etc. can be used. Especially perfluorocarbon sulfonic acid (Nafion) is excellent in chemical resistance and thermal resistance, and suitable.

[0013] Next, content of the silica in a cathode catalyst bed and an anode catalyst bed and/or a silica fiber is explained. According to this invention, the silica and/or the silica fiber contain in the cathode catalyst bed. thereby, the water generated by the electrode reaction in a cathode catalyst bed vaporizes in a gas gaseous phase -- since thing prevention can be carried out, when there are few amounts of generation of the water in a cathode, fixed moisture can be held in a fuel cell subsystem like [at the time of a halt of actuation of a cell, or low loading]. Moreover, like [at the time of a heavy load], when there are many amounts of generation of the water in a cathode, the superfluous moisture of a cathode can carry out the back diffusion of electrons to an anode side (when it is easy to generate desiccation of an anode or ion exchange membrane), and the duty as a source of ion exchange membrane and an anode can be performed. Moreover, when the silica and/or the silica fiber contain in the anode catalyst bed, while preventing desiccation of an anode, the duty which promotes the back diffusion of electrons of the moisture from a cathode side to an anode side can be performed.

[0014] Moreover, the silica contained in a cathode catalyst bed and an anode catalyst bed and/or the silica fiber are the same as what was contained in ion exchange membrane. Moreover, in order to advance electrode reaction smoothly in a catalyst bed, it is desirable to make a catalyst particle (or catalyst which deposited platinum by reduction on the carbon particle front face) / solid polymer electrolyte become the weight ratio of 1 / 9 - 5/5. By the way, since that a silica contains in 0.01 - 50% of the weight of the range to the weight of a solid polymer electrolyte can improve the specific resistance and water content of a catalyst bed as shown in Table 1, it is desirable to make the silica

which corresponds to 0.0006 - 31% of the weight to a catalyst bed contain. Moreover, as for a solid polymer electrolyte, it is desirable to use the same thing as having used for ion exchange membrane. Moreover, if a catalyst particle (or catalyst which deposited platinum by reduction on the carbon particle front face), a giant-molecule solid electrolyte, a silica, and/or a silica fiber are similarly mixed with ion exchange membrane having indicated in the condition of having made it suspending and dissolving in the solvent of hydrophilic properties, such as a methanol, ethanol, isopropanol, and a butanol, respectively when making a catalyst bed contain a silica, since the specific resistance of a catalyst bed will become small, it is desirable.

[0015] Although each effectiveness can raise the cell engine performance with the solid polymer electrolyte mold fuel cell of this invention also when a silica and/or a silica fiber contain in the one of ion exchange membrane, a cathode catalyst bed, and anode catalyst beds as explained above, containing in ion exchange membrane is desirable at least. However, the big description of the solid polymer electrolyte mold fuel cell of this invention is being able to operate by no humidifying while being able to raise the cell engine performance notably, when a silica and/or a silica fiber contain in ion exchange membrane, cathode catalyst beds, and all the anode catalyst beds. That is, by this silica content, if water is generated by the electrode reaction in a cathode catalyst bed, by the cathode catalyst bed, the vaporization to the inside of the reactant gas of generation water will be prevented, and the ion exchange membrane of the redundant water of a cathode catalyst bed and the back diffusion of electrons by the side of an anode catalyst bed will be helped. Thereby, the solid polymer electrolyte fuel cell of this invention can be operated, without the moisture in a fuel cell subsystem needing the humidification from the outside of a fuel cell subsystem, since migration and the back diffusion of electrons are performed by the closed system.

[0016] In addition, as for each content of the silica contained in ion exchange membrane, the catalyst bed for cathodes, and the catalyst bed for anodes, and/or a silica fiber, it is desirable to change within the limits of the content described above from migration of the moisture in a fuel cell subsystem and the balance of the back diffusion of electrons. For example, many silicas and/or silica fibers can be made to be able to contain in the catalyst bed side for anodes which is easy to dry, and the catalyst bed for cathodes by which water is generated can be made to contain a silica and/or a silica fiber fewer. In this case, it is also possible to make the silica and/or silica fiber of a plane of composition of an anode catalyst bed and an ion exchange membrane which were applied to the whole surface at least into the structure embedded by heating sticking-by-pressure processing of a hotpress etc. at the surface layer. It is possible similarly to make it the structure which embedded the silica and/or the silica fiber also in the plane of composition of the catalyst bed for anodes and an anode charge collector, the plane of composition of ion exchange membrane and the catalyst bed for cathodes, and the plane of composition of the catalyst bed for cathodes and cathode current collection many objects.

[0017] While the ion conductivity of the ion exchange membrane itself is improvable like the above according to the solid polymer electrolyte mold fuel cell of this invention, non-humidified operation of a solid polymer electrolyte fuel cell can be enabled.

[0018]

[Function] Since the silica and/or the silica fiber contain, respectively in the ion exchange membrane which constitutes the solid polymer electrolyte mold fuel cell of this invention, the cathode catalyst bed, and the anode catalyst bed, the ion conductivity of a cell is improved and the cell engine performance can be raised. Moreover, when water content becomes high, the moisture generated by the catalyst bed for cathodes is diffused in the catalyst bed side for anodes, and supplies moisture to ion exchange membrane and the catalyst bed for anodes. Thereby, since the moisture in a cell is moved and spread with a closed system, non-humidified operation can be performed.

[0019]

[Example 1] Next, although the desirable example of the solid polymer electrolyte mold fuel cell concerning this invention is indicated, this example does not limit this invention. The ion exchange membrane used for the solid polymer electrolyte mold fuel cell of this invention was made by the following process.

[0020] First, the isopropyl alcohol dispersion liquid (concentration -- 5 g/l) of a silica (trade name -- Aerosil 380, the product made from Japanese Aerosil, first [an average of] grain size of 0.007 micrometers) equivalent to 5 % of the weight were mixed with the 5-% of the weight isopropanol solution (Aldrich make) of Nafion to said Nafion weight, and it stirred well with the ultrasonic homogenizer. Next, reduced pressure drying was carried out by 60-degreeC, and isopropanol was removed, membranes were formed [this solution was slushed into the film molding container, and], and 5 % of the weight of silica content and the ion exchange membrane of 0.1mm of thickness were created. In addition, membrane formation by extrusion molding or screen-stencil is also possible.

[0021] Moreover, the cathode catalyst bed and anode catalyst bed which were used for the solid polymer electrolyte mold fuel cell of this invention were made from the following process. First, the catalyst which deposited platinum by reduction on the surface of the carbon particle, Nafion, and a silica mixed each ethanol solution which becomes the weight ratio of 1:1:0.05, and stirred well with the ultrasonic homogenizer. Next, after carrying out reduced pressure drying of this liquid by 60-degreeC and removing ethanol, a dry matter is crushed and it imprints to the carbon paper of a collector with a filtration replica method, and they are 130-degreeC and 5kg/cm². The hotpress was carried out for 3 seconds and it fabricated in the shape of sheet metal. The used silica is the same as what was used by said ion exchange membrane. To the weight of a catalyst bed, the silica content of the catalyst bed at this time is 2.4 % of the weight, and the cathode catalyst bed and the anode catalyst bed made it the same content.

[0022] And like the above, the created catalyst inter-electrode of two sheets pinched the ion exchange membrane created like the above, and the solid polymer electrolyte fuel cell shown in drawing 1 and drawing 2 was assembled. In drawing 1 and drawing 2, the cathode charge collector with which in 1 a cathode catalyst bed and 3 have an anode catalyst bed, and, as for 4, ion exchange membrane and 2 have the supply path 5 of oxygen, the anode charge collector with which 6 has the supply path 7 of hydrogen, and 8 show the sealant.

[0023] Moreover, as an example of a comparison, except not containing a silica, ion exchange membrane, the cathode catalyst bed, and the anode catalyst bed were produced like the above, and the solid polymer electrolyte fuel cell was assembled like drawing 2. And the comparison test shown below was carried out as the evaluation approach of the cell engine performance of the solid polymer electrolyte fuel cell of this invention, and the conventional solid polymer electrolyte fuel cell.

(1) It operated by no humidifying and the solid polymer electrolyte mold fuel cell of this invention measured specific resistance. On the other hand, the solid polymer electrolyte mold fuel cell created as an example of a comparison measured specific resistance about the case of not humidifying, when it humidified to hydrogen gas. The actuation conditions of a cell are as follows and show a comparison result to drawing 3.

[0024]

Reactant gas -- Hydrogen (anode side), oxygen (cathode side)

Cel operating temperature -- 80-degreeC humidification temperature -- 80-degreeC (when it humidifies)

Cel operating pressure -- The solid polymer electrolyte mold fuel cell of this invention is smaller than specific resistance when the solid polymer electrolyte mold fuel cell of the example of a comparison humidifies the specific resistance in spite of no humidifying, and it was shown that ion conductivity is good so that clearly from the result of atmospheric pressure drawing 3. Moreover, specific resistance when the solid polymer electrolyte mold fuel cell of the example of a comparison-less humidifies showed the clearly high value.

[0025] This also showed that, as for the solid polymer electrolyte mold fuel cell of this invention, no humidifying had the cell engine performance more than an EQC compared with the time of the solid polymer electrolyte mold fuel cell of the example of a comparison humidifying.

(2) Moreover, said both solid polymer electrolyte mold fuel cell is current density 350 mA/cm² under the conditions of not humidifying. The result of having compared the battery life at the time of operating is shown drawing 4.

[0026] The solid polymer electrolyte fuel cell of this invention is understood that the cell engine

performance is clearly high compared with the solid polymer electrolyte fuel cell of the example of a comparison so that clearly from the result of drawing 4 . Moreover, the solid polymer electrolyte fuel cell of this invention was maintaining the cell engine performance stabilized also after 500 hours in spite of non-humidified operation. From the above result, it was able to check that non-humidified operation was possible for the solid polymer electrolyte fuel cell of this invention.

[0027]

[Example 2] The ion exchange membrane which made the silica staple fiber of 3 micrometers of sizes contain 5% of the weight to the weight of said Nafion was formed by the same membrane formation approach as an example 1, and the solid polymer electrolyte mold fuel cell was made. In addition, it considered as the same configuration as the solid polymer electrolyte mold fuel cell of an example 1 except ion exchange membrane. And the specific resistance in non-humidified operation or humidification operation was measured about this solid polymer electrolyte mold fuel cell.

Consequently, the specific resistance in non-humidified operation was set to 7-ohmcm, and also when a silica fiber was made to contain, it obtained the same result as an example 1. Moreover, the specific resistance in humidification operation was able to be set to 5.5-ohmcm, and was able to obtain still smaller specific resistance.

[0028]

[Effect of the Invention] Since good moisture management can be performed according to the solid polymer electrolyte fuel cell concerning this invention when the silica and/or the fibrous silica fiber of a very fine particle contain in one of them at least among ion exchange membrane, the catalyst bed for cathodes, and the catalyst bed for anodes as explained above, cell internal resistance can be made small and high performance-ization of a cell can be attained.

[0029] When the silica and/or the fibrous silica fiber of a very fine particle contain in ion exchange membrane, the catalyst beds for cathodes, and all the catalyst beds for anodes, it can operate by no humidifying.

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MENU **SEARCH** **INDEX** **DETAIL** **JAPANESE**

1 / 1